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Development of an Electrochemical Acidification Cell for the Recovery of CO_2 and H_2 from Seawater

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ABSTRACT: Based on continuous electrodeionization (CEDI) technology, a novel hybrid electrochemical acidification process has been developed to extract large quantities of CO_2 from seawater. This indirect approach acidifies seawater to recover CO_2 from bicarbonate. The electrolytic regeneration of cation exchange resin allowed simultaneous and continuous ion exchange and regeneration to occur within the cell along with control of the seawater pH. Lowering seawater pH was found to be proportional to the applied current to the cell, and the CO_2 in the acidified seawater was readily removed at pH less than 6.0. In addition, the cell produced a portion of hydrogen gas without additional energy penalties.

INTRODUCTION

Continuous electrodeionization (CEDI) technologies are widely used to produce ultrapure water for power plants, semiconductor and chemical manufacturing processes, pharmaceutical/biotechnology industries, and academic and clinical laboratories.[1−4] In addition, CEDI technologies are finding more application in heavy metal cation and anion separations.[2,4−6] It is well-known that CEDI works on the principle of removing ionizable species from liquids by manipulating their ionic transport properties using an applied electrical potential, ion exchange resins, and semipermeable ion exchange membranes as electrically active media.[3,4,6−9] Currently, commercial water purification systems based on these principals have a capacity ranging from 0.8 to 400 000 gal/h (0.1−1500 m^3/h).[3] In efforts to take advantage of CEDI ion transport principles, system commercial availability, and capacity to process large quantities of water, a standard commercial chlorine dioxide device was modified to mimic a CEDI module and reduce seawater pH. At pH less than or equal to 6, dissolved bicarbonate and carbonate in seawater re-equilibrate to CO_2 gas.

The $[CO_2]_T$ of the world's oceans is between 2000 and 2400 μmol/kg at all depths. This is equivalent to approximately 100 mg/L of $[CO_2]_T$.[10,11] On a weight per volume basis this concentration is about 140 times greater than in air (0.7 mg/L).[12] Thus if sufficient quantities of CO_2 and H_2 could be extracted from seawater economically and efficiently, future marine engineering processes such as OTEC (ocean thermal energy conversion)[13,14] and nuclear power[15] could be envisioned to utilize these chemical feedstocks in processes such as catalytic polymerization directly to value added hydrocarbons.[16]

The challenge is developing technologies to capture sufficient quantities of carbon dioxide and hydrogen from seawater so that energy consumption is minimized. The difficulty is that seawater is a complex buffered system. Dissolved bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) species are primarily responsible for buffering and maintaining the ocean's pH which is relatively constant below the first 100 m. These dissolved bicarbonate and carbonate species are essentially bound CO_2 and their sum along with dissolved gaseous CO_2 represents the total carbon dioxide concentration $[CO_2]_T$ of seawater, eq 1.

$$\sum[CO_2]_T = [CO_2(aq)] + [HCO_3^-(aq)] + [CO_3^{2-}(aq)] \quad (1)$$

In typical seawater, approximately 2−3% of the CO_2 is dissolved gas in the form of carbonic acid (H_2CO_3), 1% is carbonate (CO_3^{2-}), and the remaining 96−97% is dissolved bicarbonate (HCO_3^-). Under equilibrium conditions dissolved $[CO_2(aq)]$ is actually hydrated with one mole of water in the form of carbonic acid as shown in eq 2. The dissolved bicarbonate and carbonate are in equilibrium with this dissolved carbonic acid species shown in eq 3.

$$[CO_2(g)]_{air} \overset{H_2O}{\rightleftarrows} [CO_2(aq)] \overset{H_2O}{\rightleftarrows} [H_2CO_3(aq)] \quad (2)$$

$$CO_2(g) \overset{H_2O}{\rightleftarrows} CO_2(aq) \overset{H_2O}{\rightleftarrows} H_2CO_3(aq) \overset{H_2O}{\rightleftarrows} 2HCO_3^-(aq) \rightleftarrows CO_3^{2-}(aq) + H_2O(l) + CO_2(g)\uparrow \quad (3)$$

The H_2CO_3 species is in equilibrium with the gas phase above the water as CO_2, and so any reduction of CO_2 partial pressure in the gas phase will cause the equilibrium of the entire system to shift to the left (eq 3).[17,18] This process is very slow and not well understood.[19] Thus only 2−3% of the $[CO_2]_T$ in seawater could be quickly recovered, but not in sufficient quantities as a chemical feedstock.

Seawater's salinity presents additional challenges in developing technologies for CO_2 capture from seawater. The salinity is

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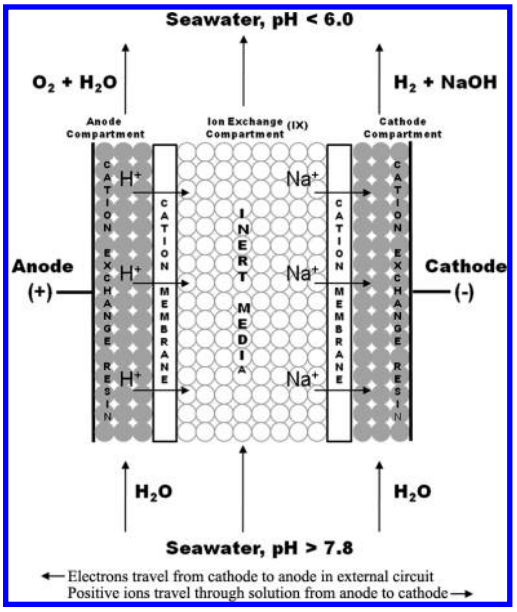

Figure 1. Electrochemical acidification cell.

approximately 35 g/L and is primarily attributed to sodium chloride. The total chloride content in seawater is about 240 times greater than the targeted bicarbonate ion.[17] In efforts to overcome these challenges, Willauer et al. investigated the feasibility of using gas-permeable membranes and simple ion-exchange resin systems as methods of recovering CO_2 from the ionic form of bicarbonate and carbonate in addition to the dissolved gas.[20−22] The permeance rates and limited fixed volume effect justify further studies involving different membrane configurations in open ocean systems.[20,21] Strong base anion exchange resins' selectivity and capacity were proven to be inefficient to acquire sufficient quantities of CO_2 as feedstock for a catalytic chemical polymerization process.[22] Strong acid cation resins were extremely successful at acidifying seawater to a pH less than 6 so the total CO_2 existed in the dissolved gas form. However regeneration required the use of hazardous acids which was deemed impractical.[22,23]

As one further possibility to exploit the pH as a means to recover carbon from the sea, a commercial chlorine dioxide generation cell was reconfigured in this study to function as an electrochemical acidification cell. This novel hybrid process takes advantage of CEDI electroregeneration mechanisms and ion transport properties to control and reduce seawater pH.[3,4,6−9] Simultaneously, the process produces hydrogen gas through electrolytic dissociation of water in the cathode compartment.[4,7] This approach described within is considerably different from traditional electrolysis methods that are specifically tailored toward the production of hydrogen and oxygen from seawater and or fresh water. Most modern military submarines generate their breathing oxygen from the electrolysis of fresh water.[24] The difficulty with current seawater electrolysis technology for hydrogen production is the formation of chlorine gas and thus electrodes are modified such that only oxygen is evolved at the anode.[25] In this study the effects of electrochemical acidification cell configuration, seawater composition, flow rate, and current on seawater pH are evaluated. In addition, the relationship between the pH of seawater and CO_2 degassing is discussed. These data are used to determine the feasibility of this approach for a carbon capture/hydrogen production process.

Table 1. Nalco Cell Configured as an Electrochemical Acidification Cell

dimensions	
approximate overall cell dimension	14.0 cm × 36.5 cm × 6.0 cm
IX compartment width	5.1 cm
IX compartment height	30.1 cm
IX compartment thickness	1.2 cm
IX compartment volume	184.2 cm^3
membranes active area	153.5 cm^2
electrode compartment volume	98.4 cm^3
electrical specification	
electrode active area	153.5 cm^2
max. current density	100 A m^{-2}
flow specification	
max. flow rate	20 cm^3 s^{-1}
max. electrolyte flow rate	10 cm^3 s^{-1}
max. operating temperature	60 °C
max. operating pressure	350 kPa
materials	
anode	dimensionally stable anode (DSA-600)
cathode	316L stainless steel
membrane	sybron cation-permeable membrane
molded frame and end block	acrylonitrile butadiene styrene (ABS)

EXPERIMENTAL SECTION

A commercial Nalco chlorine dioxide generation cell was reconfigured to operate as an electrochemical acidification cell. Figure 1 shows the three-compartment cell configuration. The central ion exchange (IX) compartment and the electrode compartments (cathode and anode) were separated by a Sybron MC-3470 reinforced/casted cation-permeable membrane. The acid functionality of the membranes provided discrete channels for Na^+ and H^+ ions to migrate through the polymer matrix while blocking the passage of anions. The anode was a dimensionally stable anode (DSA) (mixed precious metal oxide coating on titanium), and the cathode was composed of 316L stainless steel. Two different types of ion exchange media, strong cation exchange resin (IRA-120) from Rohm & Haas and inert ceramic particles, were tested in the IX compartment to evaluate and determine its effects on the exchange of Na^+ for H^+ ions in the cell. A detailed description of the cell's electrical and flow rate specifications along with the materials used in the cell's configuration are provided in Table 1.

Figure 2 is a schematic that describes the acidification experimental setup. Seawater was passed upwardly through the IX compartment. Deionzied water at a pH of approximately 6.7 and a conductivity less than 20 μS/cm was passed upwardly through the anode compartment and then upwardly through the cathode compartment in series. A controlled current was applied to the anode and cathode in order to lower the pH of the seawater to a target level. This was a single pass system, so once a volume of seawater and deionized water passed through the cell it was not utilized again in the test.

Four different synthetic seawater formulations were created from commercially available instant ocean salts (IO) used in seawater

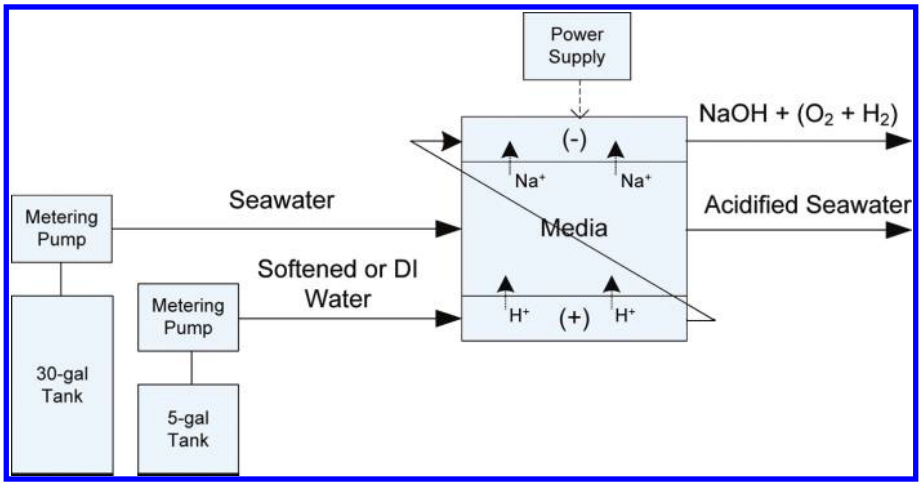

Figure 2. Schematic of electrochemical acidification experimental layout.

aquaria. The synthetic formulations were prepared 16 h prior to use to allow the buffer salts to reach equilibrium. These solutions were designated as IO1, IO2, IO3, and IO4. IO1 was prepared by dissolving 41.1 g/L of instant ocean sea salt in deionized water at a total volume of 100 L. The pH of the synthetic seawater was 9.1 ± 0.5. IO2 was prepared by dissolving 35 g/L of instant ocean sea salt in deionized water at a total volume of 140 L. The pH measured 8.4 ± 0.2. IO3 was prepared by diluting 35 g/L instant ocean sea salt and 90 mg/L sodium bicarbonate in deionized water to 140 L. The pH measured 8.3 and the $[CO_2]_T$ content measured by coulometry was 100 mg/L. IO4 was the same seawater formulation as IO3, but the pH of IO4 was adjusted to 7.6 using hydrochloric acid (HCl). The $[CO_2]_T$ content of this solution measured 100 mg/L by coulometry. Key West seawater was obtained from the Naval Research Laboratory Key West, Florida facility. The pH was 7.6 ± 0.2 and the $[CO_2]_T$ content was measured to be approximately 100 mg/L by coulometry. All coulometric measurements were made by a UIC Coulometric system (UIC Inc., Joliet, IL).[26] The pH of the solutions varied as a result of equilibration with CO_2 gas in the atmosphere. These pH changes had no effect on the overall performance of the acidification cell. All pH measurements were conducted with a standardized Fisher combination glass electrode.

Degassing measurements were made on selected samples during the course of the experiment. For each measurement the carbon dioxide was degassed from solution using a Brinkmann Roto-Evaporator. A 20-mL sample was placed in a 1000-mL round-bottom flask and rotated at an rpm setting of eight for 5 min. A water aspirator provided a vacuum of approximately 2 kPa (15 mmHg). The $[CO_2]_T$ content of the samples were measured by coulometry.

RESULTS AND DISCUSSION

The acidification of seawater offers an indirect approach to recovery of CO_2 in its bicarbonate form from the equilibrium conditions of CO_2 in seawater shown in eq 4.[23] Johnson et al. demonstrated that carbonate and bicarbonate re-equilibrate to CO_2 gas at seawater pH less than or equal to 6 (eq 4).[26] Removal of CO_2 gas was possible by vacuum or air sparging. This method has been the basis for standard quantitative ocean CO_2 measurements for over 25 years.

$$HCO_3^- + H^+ \rightleftarrows H_2CO_3 \rightleftarrows H_2O + CO_2(g)\uparrow \quad (4)$$

The chlorine dioxide cell reconfigured to operate as an electrochemical acidification cell used small quantities of electricity to exchange Na^+ ions for H^+ ions in the seawater stream flowing between the two cation exchange membranes (Figure 1). At the anode, H^+ ions were generated by the oxidation of deionized water and this oxidation was proportional to the applied electrical current and voltage. The current drove the H^+ ions from the surface of the anode, through the cation-permeable membrane, and into the IX compartment where they replaced the sodium ions in the flowing seawater. As a result the effluent seawater was acidified. Sodium ions were transferred through the membrane closest to the cathode and removed from the seawater by means of direct current (DC) voltage. The acid functionality of the membranes provided discrete channels for cations to migrate through the polymer matrix while blocking the passage of anions. The anolyte had to be as dilute as possible such that H^+ were in excess and did not compete with any other cations. The catholyte was deionized water since it had to be free from hardness ions calcium (Ca^{2+}) and magnesium (Mg^{2+}) since the pH in the cathode compartment was high enough to precipitate these hardness ions out of solution and onto the cathode itself.

Depicting seawater by sodium chloride (NaCl) and acidified effluent seawater by HCl, the reactions within the electrochemical acidification cell are as follows:

$$\text{Anode}: \ 2H_2O \rightarrow 4H^+ + O_2 + 4e^- \quad (5)$$

$$\text{IX}: \ 4|NaCl|_{Seawater} + 4H^+ \rightarrow 4Na^+ + 4|HCl|_{AcidicSeawater} \quad (6)$$

$$\text{Cathode}: \ 4H_2O + 4Na^+ + 4e^- \rightarrow 4NaOH + 2H_2 \quad (7)$$

$$\text{Overall}: \ 6H_2O + 4NaCl \rightarrow 4|HCl|_{IX} + 4|NaOH| + 2|H_2|_{Cathode} + |O_2|_{Anode} \quad (8)$$

The amount of H^+ generated is proportional to the applied electrical current which follows Faraday's constant. Faraday's

Table 2. Test 1: Acidification of IO1 pH = 9.1 at 140 mL/min Using Strong Acid Ion Exchange Resin in the IX Compartment

time, min	amp/volt	influent seawater flow rate, mL min^{-1}	influent DI flow rate, mL min^{-1}	effluent acidified seawater pH	effluent DI cathode pH
15	3.0/9.0	150	80	2.08	12.69
30	3.0/10.0	140	77	-	-
45	3.0/10.0	140	75	2.15	12.63
60	3.0/11.0	140	75	2.10	12.49
75	3.0/12.0	140	144	-	-
90	2.0/9.0	140	140	2.19	12.13
105	1.0/6.0	140	140	2.70	12.00
120	0.5/4.0	140	140	3.61	11.41
135	0.25/3.0	140	140	5.88	11.26
150	0.0/0.0	140	140	-	-
165	0.0/0.0	140	140	8.76	10.41

Table 3. Test 2: Acidification of IO2 pH = 8.4 at 900 mL/min Using Strong Acid Ion Exchange Resin in the IX Compartment

time, min	amp/volt	influent seawater flow rate, mL min^{-1}	influent DI flow rate, mL min^{-1}	effluent acidified seawater pH	effluent DI cathode pH
15	1.0/5.0	900	140	7.31	11.79
30	1.5/7.0	900	140	6.13	12.06
45	1.5/7.0	864	140	5.95	12.04
60	1.5/7.0	870	140	4.63	11.90
75	1.5/7.0	864	140	4.41	11.89
90	1.5/7.0	868	140	4.30	11.75
105	1.5/7.0	860	140	4.18	11.76
120	1.5/7.0	860	140	4.05	11.74
135	1.0/6.0	860	140	6.31	11.12
150	1.0/6.0	860	140	6.20	11.42
165	1.0/6.0	860	140	6.27	11.52
180	1.2/6.5	860	140	6.17	11.20

constant is defined as the amount of electricity associated with one mole of unit charge or electron, having the value 96 487 A second/equivalent. For the anode reaction 96 487 A sec will produce $^1/_4$ mol O_2 gas and 1 mol H^+, and for the cathode reaction 96 487 A sec will produce $^1/_2$ mol H_2 gas and 1 mol OH^-. This allows the amount of H^+, OH^-, H_2, and O_2 produced per amp/second of current passed through the electrodes to be determined as follows:

Anode Reaction

$$\left(\frac{1/4\ \text{mole}O_2}{96,487\ \text{A sec}}\right)\left(\frac{60\ \text{sec}}{\text{min}}\right) = 0.000155\frac{\text{mole}O_2}{\text{A min}} \quad (9)$$

$$\left(\frac{1\ \text{mole}H^+}{96,487\ \text{A sec}}\right)\left(\frac{60\ \text{sec}}{\text{min}}\right) = 0.000622\frac{\text{mole}H^+}{\text{A min}} \quad (10)$$

Cathode Reaction

$$\left(\frac{1/2\ \text{mole}H_2}{96,487\ \text{A sec}}\right)\left(\frac{60\ \text{sec}}{\text{min}}\right) = 0.000311\frac{\text{mole}H_2}{\text{A min}} \quad (11)$$

$$\left(\frac{1\ \text{mole}OH^-}{96,487\ \text{A sec}}\right)\left(\frac{60\ \text{sec}}{\text{min}}\right) = 0.000622\frac{\text{mole}OH^-}{\text{A min}} \quad (12)$$

Therefore, for a seawater solution with a HCO_3^- concentration of 0.0023 M and flow rate of 1 L per minute, a theoretical applied current of 3.70 A will be required to lower the pH to less than 6.0 and convert HCO_3^- to H_2CO_3.

$$\frac{\left(\frac{0.0023\ \text{mole}HCO_3^-}{\text{liter}}\right)\left(\frac{1\ \text{liter}}{\text{min}}\right)}{\left(\frac{0.000622\ \text{mole}H^+}{\text{A min}}\right)} = 3.70\ \text{A} \quad (13)$$

The theoretical maximum amount of CO_2 that can be removed from the acidified seawater is 0.0023 mol per liter. Removal efficiency can be defined as the ratio of the theoretical amount of CO_2 removed to the actual amount of CO_2 removed in the acidified seawater. The theoretical amount of H_2 gas generated at 3.7 A is

$$\left(\frac{1/2\ \text{mole}H_2}{96,487\ \text{A sec}}\right)\left(\frac{60\ \text{sec}}{\text{min}}\right)(3.70\ \text{A}) = 0.0011\frac{\text{mole}H_2}{\text{min}} \quad (14)$$

Increasing the current increases the molar ratio of the measured hydrogen to carbon dioxide with no effect on the operation of the acidification cell. H^+ generated will either exchange with Na^+ in the seawater to further lower its pH or migrate through the IX compartment and into the cathode compartment where it will combine with OH^- to form water.

The electrochemical acidification cell in the first test of this series of feasibility studies was configured such that strong acid cation exchange resin filled both the IX compartment and the electrode compartments. IO1 seawater was used as the influent and passed through the IX compartment at a flow rate of 140 mL/min for 165 min. The deionized water rate through the electrode compartments was increased to a final flow rate of 140 mL/min. The results summarized in Table 2 show that when 3 A were applied to the cell, the pH of the effluent seawater was between 2.08 and 2.15. As the current was decreased from 3 to 0.25 A, the pH of the effluent seawater was increased to 5.88. These results demonstrate that the pH of the effluent seawater can be lowered using the acidification cell as it is configured and it is proportional to the applied current. The results suggest the electrolytic regeneration of the cation exchange resin. The seawater flow rate to current ratio when the seawater pH was 5.88 is estimated to be 560 (140 mL/min/0.25 A). This ratio is higher than the theoretical ratio of 269 calculated for the same conditions as described by eq 13 (1000 mL/min/3.70 A = 140 mL/min/X and X = 0.52 A so the theoretical ratio was 140 mL/min/0.52 A = 269). This ratio is a sizing parameter to use for scaling up the process. In addition it may be related to current efficiency at common seawater effluent pH. Thus the higher ratio of 560 indicates that the HCO_3^- levels in the IO1 synthetic formulation may be lower than that measured in natural seawater even though the pH of IOI measured 9.1.

The recovery was at 50% and not varied in this experiment. The term "recovery" is used to define the ratio of product quantity (influent seawater flow rate, Table 2) over the total feed quantity to the cell (influent seawater flow rate plus influent deionized flow rate, Table 2) as a percent. This is critical since the water required in the electrode compartments must be dilute and free from hardness ions. This type of water must be treated by a

Table 4. Test 3: Acidification of IO2 pH = 8.4 at 680 mL/min Using Inert Material in the IX Compartment

time, min	amp/volt	influent seawater flow rate, mL min^{-1}	influent DI flow rate, mL min^{-1}	effluent acidified seawater pH	effluent DI cathode pH
15	1.0/8.0	680	140	8.29	11.88
30	1.0/8.0	680	140	8.48	11.88
45	1.0/8.0	680	140	8.28	11.87
60	1.0/8.0	680	140	7.13	11.87
75	1.0/8.0	680	140	6.62	11.90
90	1.0/8.0	680	140	6.10	11.88
105	1.0/8.0	680	140	5.51	11.88
120	1.0/8.0	680	140	4.22	11.52
135	1.0/8.0	680	140	6.46	11.25
150	0.8/6.0	680	140	6.30	11.33
165	0.9/6.5	680	140	5.87	11.36
180	0.9/7.0	680	140	5.83	11.42

Table 5. Test 4: Acidification of IO2 pH = 8.4 at 140 mL/min Using Inert Material in the IX Compartment

time, min	amp/volt	influent seawater flow rate, mL min^{-1}	influent DI flow rate, mL min^{-1}	effluent acidified seawater pH	effluent DI cathode pH
60	0.178/4.75	140	18	3.96	10.82
120	0.169/4.63	140	16	4.19	10.92
180	0.136/4.27	140	17	5.30	10.84
240	0.116/4.03	140	18	6.07	10.82
300	0.116/3.99	140	17	5.75	10.92
360	0.116/3.91	140	10	5.92	10.84
420	0.116/3.79	140	10	5.88	10.88

filtration process such as reverse osmosis. A high recovery will allow the size of the filtration unit along with the energy requirements for the unit to be minimized.

In the second test, a similar IO synthetic formulation was made (IO2) and used to determine the effect that flow rate through the IX compartment had on the performance (Tables 3, 4, and 5). Initially IO2 was pumped at 900 mL/min before a flow of 860 mL/min was established and maintained after 90 min. The results summarized in Table 3 establish that at higher flow rates the pH of the effluent seawater can be lowered using the acidification cell. Higher influent seawater flow rates increase the percent recovery from 50% to 86%. In addition the results suggest that the seawater flow rate to current ratio was improved from 560 to 716 (860 mL/min/1.20 A).

The strong acid cation exchange resin material in the IX compartment of the cell was replaced in the third test with inert ceramic particles. The effect of the ceramic media on the substitution of Na^+ by H^+ ions was evaluated and the results are shown in Table 4. At a flow rate of 680 mL/min to the IX compartment and an applied current of 1.0 A, the pH of IO2 is reduced from 8.29 to 6.3 in 150 min. Because the pH of the IO2 water can be lowered with the inert media in the IX compartment the process is considered to be an electrically driven membrane process. The progressive decrease in the IO2 pH indicates that the cation exchange resin in the anode compartment

Table 6. Test 5: Acidification of KW pH = 7.6 Seawater at 140 mL/min Using Inert Material in the IX Compartment

time, min	amp/volt	influent seawater flow rate, mL min^{-1}	influent DI flow rate, mL min^{-1}	effluent acidified seawater pH	effluent DI cathode pH
1	0.15/3.14	140	10	5.52	-
2	0.15/3.13	140	10	6.05	-
3	0.15/3.14	140	10	6.14	-
4	0.15/3.14	140	10	6.23	-
5	0.15/3.14	140	10	6.29	
6	0.17/3.21	140	10	6.35	-
7	0.17/3.23	140	10	6.35	-
9	0.19/3.37	140	10	6.42	-
11	0.21/3.45	140	10	6.42	-
13	0.26/3.61	140	10	6.37	-
15	0.31/3.84	140	10	-	-
17	0.40/4.06	140	10	6.20	-
19	0.47/4.33	140	10	6.09	-
21	0.47/4.34	140	10	6.04	-
23	0.47/4.33	140	10	5.97	-

was regenerating. Because the cation exchange resin in the anode compartment was in the sodium form during the start of the experiment, H^+ ions from the oxidation of water on the anode exchanged on the resin and released Na^+ ions. These Na^+ ions then migrated through the cation exchange membrane and into the IX compartment. Breakthrough of H^+ ions into the IX compartment began at 60 min when the pH of the seawater began to decrease. See Figure 1 for illustrative details. Finally the Na^+ migrate into the cathode compartment, resulting in a high and stable pH due to the formation of NaOH. In addition to the electrically driven membrane process, the flow rate to current ratio was further improved from 716 to 755 (680 mL/min/0.90 A) at a recovery of 83%.

When the flow rates to the IX compartment and the electrode compartments were dropped from 680 to 140 mL/min in the IX compartment and from 120 to 18 to 10 mL/min in the electrode compartments in the fourth test shown in Table 5, there was an improvement in the flow rate to current ratio to 1207 (140 mL/min/0.116 A). In addition, the lower flow rates to the cell increased the recovery from 88 to 95%.

With the optimum cell configuration and flow rates established by previous experiments, Key West seawater was used in order to simulate sample conditions that would be encountered in an actual ocean process for recovery of CO_2. The results summarized in Table 6 show the flow rate to current ratio was significantly reduced to approximately 298 (140 mL/min/0.47 A). This ratio is very similar to the theoretical ratio of 269 (140 mL/min/0.52 A (eq 13)), and the recovery was at 94%.

The CO_2 content of the KW seawater measured approximately 100 mg/L by coulometry. Table 6 shows that it required 0.47 A to decrease the pH of the Key West seawater to 5.97. This is approximately 4 times more current than was needed in the previous experiment using IO2 seawater. This can be explained by the $[CO_2]_T$ content of Key West seawater. Approximately 97% of the $[CO_2]_T$ in seawater is attributed to bicarbonate, and the acidification cell is producing carbon dioxide from its bicarbonate form (eq 4). As a result, the higher the bicarbonate concentration of the water, the more current needed to acidify

Table 7. Test 6: Acidification of IO3 pH = 8.2 at 140 mL/min Using Inert Material in the IX compartment

time, min	amp/volt	influent seawater flow rate, mL min^{-1}	influent DI flow rate, mL min^{-1}	effluent acidified seawater pH	effluent DI cathode pH
15	0.46/4.58	140	10	6.52	-
30	0.48/4.89	138	9	6.42	-
45	0.49/4.71	140	18	6.48	-
60	0.49/4.69	138	9	6.78	-
75	0.51/4.79	140	9	6.65	
90	0.65/5.31	139	8	6.48	-
105	0.72/5.66	140	18	6.36	-
120	0.99/6.74	140	18	6.24	-
135	1.12/7.27	140	19	6.10	-
150	1.26/7.90	140	19	5.94	-
165	1.44/8.46	140	19	5.78	-
180	1.66/9.75	140	18	5.57	-
195	1.99/12.17	140	18	5.14	-
225	1.99/12.06	140	9	5.03	-
255	1.31/9.77	140	9	5.86	-

Table 8. Test 7: Acidification of IO4 pH = 7.8 at 140 mL/min Using Inert Material in the IX Compartment

time, min	amp/volt	influent seawater flow rate, mL min^{-1}	influent DI flow rate, mL min^{-1}	effluent acidified seawater pH	effluent DI cathode pH
15	1.33/12.23	140	9	3.42	-
30	0.97/10.51	140	9	5.57	-
45	0.88/9.89	140	9	6.11	-
75	0.89/10.20	140	9	6.03	-
105	0.89/10.50	140	9	6.09	
135	0.89/10.88	140	19	6.19	-
210	1.51/13.79	140	19	2.76	-
255	1.15/12.43	140	19	4.42	-

the water (eq 13). This along with the flow rate to current ratio of 269 led to proposing that IO2 seawater contained 4 times less HCO_3^- than Key West seawater. Thus a third IO solution was prepared to have a similar alkalinity concentration as that found in KW seawater. However, the pH of IO3 was 8.19 compared to 7.67 measured for KW seawater. Table 7 shows that the amount of current required to reduce the pH of IO3 from 8.19 to 6.0 was approximately three times higher than that seen in previous test. The flow rate to current ratio was approximately 111 (140 mL min^{-1}/1.26 A), which is lower than the theoretical ratio of 267. The recovery was between 88 and 95%. The CO_2 content in IO3 was found to be adequate so the low ratio may also be associated with the acidification cell not operating long enough to reach equilibrium.

A new IO formulation for Test 7 was made in an effort to create a synthetic system that had a pH and alkalinity similar to KW seawater used in this test series. When IO4 was used to challenge the acidification cell, the results shown in Table 8 indicate that the amount of current required to reduce the pH to 6.0 was approximately two times higher (0.47 vs 0.89 A). The flow rate to current ratio was approximately 157 (140 mL/min/0.89 A), which is lower than the theoretical ratio of 267. The recovery at these flow rates was between 88 and 95%. The CO_2 content in IO4 was found to be adequate so the low ratio may be associated with the acidification cell not operating long enough to reach equilibrium. Also another explanation involves the higher voltage used in test 7 (Table 8) than in test 5 (Table 6). When this is taken into account the current to achieve a similar lower pH is very similar.

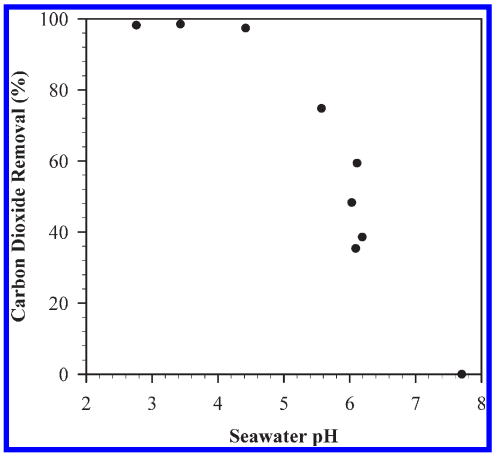

Figure 3. CO_2 Degassed Samples from Test 7 (●) Table 8.

The pH of the effluent acidified seawater was measured for each of the tests in the test series. In Test 7, the effluent acidified seawater was collected and 20-mL aliquots were placed in a 1000-mL round-bottom flask and degassed using a Brinkmann Roto-Evaporator. The $[CO_2]_T$ was measured for each solution by coulometry and plotted as a function of pH, as shown in Figure 3.

In the test, greater than 98% carbon dioxide removal was achieved at pH less than or equal to 4.5. As previously mentioned, CO_2 dissolved in water is in equilibrium with H_2CO_3 (see eqs 2 and 4). The hydration equilibrium constant (1.70×10^{-3}) indicates that H_2CO_3 is not stable and readily dissociates at pH of 4.5, allowing CO_2 to be easily removed by degassing. This was observed during all of the experiments.

CO_2 in seawater samples of pH of less than 4.5 were spontaneously and completely degassed upon exiting the acidification cell (exposed to atmosphere during sampling). CO_2 content and pH were measured before and after vacuum degassing and there was no significant difference in these two measurements.

CO_2 in seawater samples of pH greater than 4.5 required assistance by vacuum degassing for complete removal of the CO_2. In these samples, CO_2 content and pH were measured before and after vacuum degassing and there were significant differences in both measurements; CO_2 content decreased and pH increased. Although not quantified, it appeared that the level of vacuum degassing required increased as seawater pH increased.

■ CONCLUSIONS

A novel process has been developed to electrochemically acidify seawater. The electrochemical acidification cell was challenged with both synthetic seawater and Key West seawater to determine if it could be used as a feasible and practical method for extracting large quantities of CO_2 from seawater rapidly and efficiently. KW seawater simulates sample conditions that will be encountered in an actual ocean process for recovering CO_2. This acidification process converts bicarbonate in seawater to the easily recovered

CO_2(aq) form. During the experiments the electrolytic production of acid was demonstrated, allowing the simultaneous and continuous ion exchange and regeneration to occur within the cell. This eliminates the need for regeneration by hazardous acids that are not ideal for a sea-based application. The degree of ion exchange and regeneration within the cell was a function of the current and voltage applied. Lowering the pH of seawater by the acidification cell was found to be an electrically driven membrane process, where seawater effluent pH is proportional to applied current and independent of the media contained within the IX compartment. The studies showed that carbon dioxide was readily removed from seawater at pH less than 6.0. Spontaneous and nearly complete degassing was observed in seawater samples of pH of 5.0 and less. Assisted degassing by vacuum was required in seawater samples at pH greater than 5.0. The relationship between seawater bicarbonate concentration, applied current, and seawater pH followed theory when the Key West seawater was electrically acidified. The experimental setup did not allow for recoveries of greater than 95%. It is important to know the upper limit since resources (space and energy) are required to produce a dilute water stream for the electrode compartments.

The production of hydrogen gas at the cathode as a byproduct was not measured in this study. However since the amount of H_2 produced at the cathode is proportional to the applied current (equation11), presumably the applied current to the cell can be increased to generate even more hydrogen gas. The effect of increased current on cell performance and operation will be evaluated in the future. The cell's ability to produce a portion of the hydrogen needed as a feedstock would reduce operational footprint of the entire process, thus making the technology potentially more feasible.

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